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# Multi-End-Functionalized Polymers: Additives to Modify Polymer Properties at Surfaces and Interfaces

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ABSTRACT: An ongoing challenge in polymer science is the preparation of materials with specific surface properties which differ from that of the bulk, for example, hydrophobicity, wettability, chemical resistance, adhesion, or biocompatibility, while retaining the advantageous mechanical properties of the bulk polymer. We have explored the use of multi-end-functionalized polymer additives which undergo rapid adsorption to a surface or interface as an efficient method of modifying surface properties. Aryl ether moieties bearing up to four $C_8F_{17}$ groups have been used as initiators in the copper-mediated living radical polymerization of both styrene and methyl methacrylate, and the resulting polymers have been used as additives to render the surfaces of the corresponding bulk polymers hydrophobic and oleophobic. When such an additive consisting of a polystyrene chain with a molecular weight of ∼10 000 g mol$^{-1}$ end-capped with four $C_8F_{17}$ groups is present (in a matrix of polystyrene) at levels between 5 and 10 wt %, near PTFE-like surface properties result.

## Introduction

There are many occasions where it is desirable for the properties at the surface of a polymer to be distinctly different from the bulk properties. Surfaces to promote adhesion, wettability, biocompatibility, chemical resistance, and hydrophobicity are all sought after for numerous applications, and the introduction of such properties is often achieved via a costly postprocessing procedure. This may involve the application of a surface coating layer or chemical modification of the surface. Fluorinated polymer surfaces are particularly appealing in terms of their liquid repellence, chemical inertness, and low coefficient of friction. Imparting these attributes to a surface can result in the polymers finding use in applications such as antifouling finishes, biomedical devices, release coatings, and filter media.[1] Examples of current methodologies for fluorinating polymer surfaces include plasma treatments,[1−4] wet chemical modification,[5−7] and the application of polymeric surface coatings.[8,9] All or most of these approaches tend to suffer from (at least one of) being expensive, restricted to batch processing, safety hazards, or the generation of large volumes of solvent waste.

With this in mind, a number of alternative strategies have been devised for managing the surface properties of polymeric materials, one of which is the use of polymer additives which preferentially/spontaneously adsorb to the surface. However, surface adsorption will be only be spontaneous if there is an accompanying reduction in the surface energy, and as such it is therefore relatively straightforward to increase the hydrophobicity of polymer surfaces by the use of polymers functionalized with low surface energy fluorocarbon (CF) groups. This is an approach that has been demonstrated previously using fluorine-containing polymers of varying structures and with varying degrees of success.[10−45] Although it is also possible to modify surface properties by the incorporation of low molecular weight/oligomeric molecules, such additives are likely to compromise the bulk physical properties and, because they are not strongly bound to the bulk polymer matrix, may be removed by evaporation, dissolution, or wear. Durability of surface properties in some applications will be of paramount importance. In a novel approach to making polymeric materials with low surface energy, Wooley has prepared a series of hyperbranched fluorinated polymers, copolymers, and hyperbranched fluoropolymer−poly(ethylene glycol) amphiphilic networks[10−15] with antifouling and foul release coatings. A concept that has been investigated extensively with a view to managing the hydrophobicity of polymer surfaces is the use of block copolymers comprising of one block containing fluorinated groups.[16−29] In many cases the use of such block copolymers results in dramatically altered surface properties, and of particular note is the work of Ober and Kramer, who synthesized and characterized a series of poly(styrene-*b*-1,2/3,4-isoprene) block copolymers in which the isoprene units were hydroxylated and reacted with semifluorinated monodendrons carrying one, two, or three semifluorinated side groups.[18,24] It is reported that the surface of films of these block copolymers is largely made up of a uniform $-CF_3$ layer, and the surface is stabilized by the liquid crystalline behavior of these polymers which confers resistance to reconstruction of the surface layer in water even with hydrophilic groups lying just beneath the surface. Contact angles with water were highest (124° (advancing) and 110° (receding)) and surface stability greatest where the monodendron side group carried three semifluorinated groups. In these polymers the length of the polyisoprene block was ∼100 repeat units, and the extent of attachment of the semifluorinated monodendrons to the isoprene was up to 58.5%; i.e., 58.5% of the isoprene units were decorated with monodendrons. Furthermore, this work was extended to demonstrate that such block copolymers were effective for the modification of surface properties of a thermoplastic elastomer, poly(styrene-*b*-ethylene butylene-*b*-styrene) (SEBS), when added either as an additive or as a surface coating.[24] Advancing contact angles with water of 104° for the SEBS polymer itself were improved to 115° for a blend containing 10% of additive block copolymer decorated with monodendrons carrying three semifluorinated side groups. It was reported that below a blend composition of 10% the

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surface was patchy and covered with islands of additive. However, as the concentration of additive in the blend increases, there is a concomitant increase in surface coverage. The semifluorinated block copolymers performed far better when applied as a coating rather than as an additive; a coating thickness of as a little as 15 nm resulted in advancing contact angles of 125°. That the semifluorinated block copolymers are less effective at modifying the surface properties of SEBS when used as additives is due to the molecular weight and architecture of the block copolymers. As alluded to by Ober and Kramer,[24] their use as an additive relies on the surface segregation of the block copolymers to the air−polymer interface, and the kinetics of surface segregation comes into play; self-organization of the additive block copolymers in the bulk is unavoidable and will significantly retard surface segregation, and even annealing the films for several hours at 150 °C was not enough to allow sufficient diffusion of the block copolymers from the bulk to the surface to give uniform coverage.

In light of the apparent constraints associated with the use of block copolymers as additives, an alternative and attractive strategy for modifying surface properties is the use of end-functionalized polymer chains as additives which preferentially/spontaneously adsorb to the surface. It has been shown that addition of a single CF group at a polymer chain end is sufficient to lead to surface adsorption, but the effect on surface properties is modest. Previous work in our group, using polystyrenes end-functionalized with a single $C_6F_{13}$ group, failed to achieve any measurable change in contact angle with water as the contact fluid.[30] A similar study[31] using low molecular weight polystyrene additives (ca. 7000 g mol$^{-1}$) and a single $C_6F_{13}$ end group in a blend with high molecular weight unmodified polystyrene showed evidence of surface segregation and modest increases in contact angle with water from 91° to 93−94°. A number of teams have investigated the use of multiple CF end groups; Koberstein et al.[39,40] have shown that surface segregation and surface functional group concentration (versus bulk concentration) increases dramatically when two adjacent CF end groups are present at a chain end. Hirao[41−44] has prepared polystyrene polymers by anionic polymerization end-capped with up to 32 $C_8F_{17}$ groups by a methodology that involved many reaction steps. When these end-capped polymers (unblended) were cast into films, it was found, not surprisingly, that the $C_8F_{17}$ groups segregated readily to the surface and that surface segregation was strongly dependent on the number of CF groups, the alignment of the CF groups, and the linkage between the CF group and the main chain. Furthermore, XPS and static contact angle measurements suggest surface saturation of end-functionalized polymer chains in most cases when the number of CF groups reaches between 8 and 16, depending upon the particular geometry of the head group. In one case surface saturation occurred with as few as four CF groups. Static contact angle measurements of these films when the surface is saturated with CF groups were between 110° and 115° with water and between 53° and 56° with dodecane. These values are approximately what one would expect for contact angles between PTFE and the same contact liquids. More recently, Zhang et al.[45] used a fluorinated initiator, (perfluorononenyloxy)benzenesulfonyl chloride, for the controlled radical polymerization of styrene. A blend comprising of a low molecular weight polystyrene ($M_n = 3100$ g mol$^{-1}$) end-capped with this fluorinated group and unmodified polystyrene ($M_n = 10\,000$ g mol$^{-1}$) rendered the surface of solvent-cast films of the blend; hydrophobic and contact angles with water of 104° are quoted. From these previous studies it becomes apparent that although the use of CF groups at the chain end of a polymer is an effective way of rendering surfaces more hydrophobic and even to give PTFE-like surface properties, it would seem likely the use of end-functionalized polymers as additives may be a more efficient approach to modify the surface properties of polymers than the use of block copolymers, not only in terms of the number of fluorinated groups required to significantly modify surface properties, end-functionalized polymers using significantly fewer fluorinated groups, but also in terms of the rate of surface segregation. There are numerous parameters that determine the relative effectiveness of the end-functionalized polymers, including the molecular weight of the pendant polymer chain, the number and size of the CF groups, and the geometry of the head group.

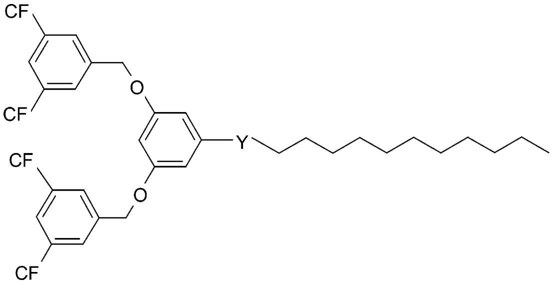


**Figure 1.** Generic structure of multi-end-functionalized polymer additive.

With this in mind we have devised a structure in which we can readily modify and control each of these parameters with dual aims of (i) ease of synthesis and (ii) of developing the optimal structure for efficient surface modification. Furthermore, bearing in mind that one of the determining factors in the effectiveness and permanence of a polymeric additive in a bulk polymer is compatibility,[46] we have endeavored to design a generic approach for maximum versatility to allow incorporation of such additives into the widest variety of polymer matrices, and the common structure we have adopted is shown in Figure 1. This common structure consists of three distinct components: a low generation (G0 or G1) dendron head group (G1 in Figure 1) carrying a predetermined number of fluoroalkyl groups (2, 3, or 4); a linking group, Y, at the focus of the dendron which can be modified to allow the attachment of a range of pendant polymer chains via a variety of mechanisms. The intended role of this pendant polymer chain is to provide long-term durability for the modified surface through chain entanglement with the bulk subphase. It is therefore a requirement that the pendant chain be at least compatible with the bulk phase and preferably of the same polymer type. The ability to attach the head group to the maximum number of polymer types is also a principal objective of this work.

Structures of this type, a linear−dendron block copolymer, have been previously reported in the literature,[47−51] and in one case[47] dendrons decorated with various functionalities including esters and carboxylic acids have been reported as “functional polymers to control surfaces and interfaces”, although no data on surface properties were reported.

We describe here the synthesis of G0 and G1 aryl ether dendrons carrying from 2 to 4 $C_8F_{17}$ fluoroalkyl groups and their use as initiators for the controlled polymerization of styrene and methyl methacrylate by copper-mediated living radical polymerization to yield polymer additives, of various molecular weights, with the aim of modifying the surface properties of bulk polystyrene and poly(methyl methacrylate). We include examples of kinetic plots of the propagation to demonstrate the degree of livingness of the polymerizations and static contact angle measurements with both water and dodecane to demonstrate the effect of the additives upon surface properties. We have further investigated both the effect of annealing and molecular weight of additive on surface segregation and surface properties and have carried Rutherford backscattering analysis to quantify the concentration of fluorine at the surface with respect to blend composition.

## Experimental Section

**Materials.** 3,5-Dihydroxybenzyl alcohol (99%), methyl 3,4,5-trihydroxybenzoate (98%), LAH (1.0 M in THF), anhydrous $K_2CO_3$ (99.995%), 18-crown-6 (99%), $CBr_4$ (99%), $PPh_3$ (99%), 2-bromoisobutyryl bromide (98%), triethylamine (99.5%), Cu(I)-Br (99.999%), and 2,2′-dipyridyl (99%) (all from Aldrich) were used as received. *N*-(*n*-Propyl)-2-pyridylmethanimine (Warwick Effect Polymers, UK) and 3-(perfluorooctyl)propanol (Fluorochem) were not purified before use. Styrene-$d_8$ (Cambridge Isotope Laboratories, 98%) was distilled, and methyl methacrylate (Aldrich, 99%) was passed over a short column of basic alumina before use.

**Measurements.** NMR spectra were recorded on a Bruker Avance-400 spectrometer. Molecular weights of polymers were determined using a Viscotek TDA 302 with refractive index, viscosity, and light scattering detectors and 2 × 300 mL PLgel 5 $\mu$m mixed C columns. THF was used as the eluent at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. Molecular weight data were obtained using a conventional calibration method generated from the appropriate standards, i.e., polystyrene samples analyzed relative to polystyrene standards and PMMA samples analyzed relative to PMMA standards. All narrow molecular weight standards purchased from Polymer Laboratories.

**Preparation of Thin Films.** Polystyrene blends were prepared by codissolving dendron-functionalized (deuterated) polystyrene and hydrogenous unmodified polystyrene ($M_n = 250\,000$ g mol$^{-1}$, $M_w/M_n = 1.05$) in toluene. Hydrogenous PMMA blends were prepared by codissolving dendron-functionalized and unfunctionalized PMMA ($M_w = 49\,000$ g/mol, $M_w/M_n = 1.02$) in toluene. Spin-coating of blended polymer solutions was carried out using a Cammax PRS14E photoresist spinner. Polymer solutions were spin-coated onto glass slides, and films of ~150 nm total thickness were obtained. Annealing of films was carried out at 160 °C for polystyrene and 150 °C for PMMA for 1 h under vacuum.

**Ion Beam Analysis.** The near-surface concentration of fluorocarbon was quantified directly by Rutherford backscattering (RBS). This technique is discussed in greater detail elsewhere.[52,53] A 1.8 MeV $^4He^+$ beam was brought onto the sample surface at a grazing incidence of 7°. Backscattered $^4He^+$ ions were detected with 19 keV resolution using a PIPS detector at 170° to the incident beam. The depth resolution at the surface of a polymer film with these settings technique is ~6 nm. Since fluorine is more massive than either C or O, $^4He^+$ recoils are detected at higher energy than recoils from these elements and are therefore easy to resolve. Halogenated organic materials are known to be quite unstable with respect to beam damage; therefore, care was taken to minimize the exposure of any single point of the sample surface to the ion beam. The beam charge on each spot was restricted to 0.5 $\mu$C, and samples were cooled to below −50 °C to minimize degradation. By summing data from at least 12 measurements on separate spots, sufficiently good statistical quality was obtained to analyze the near surface fluorocarbon distribution. Previously, we have established that this procedure is sufficient to quantify fluorinated adsorbates on polymer films.[54]

**Contact Angle Measurements.** Static contact angles were measured at room temperature using a Ramé-Hart goniometer model 100. Angles were measured for annealed and unannealed films using water and dodecane, and all data quoted is the average of at least three separate measurements.

**3-(Perfluorooctyl)propyl Bromide (1).** Compound **1** was prepared from 3-(perfluorooctyl)propanol according to the procedure reported in literature.[43] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.19 (m, 2H, $CH_2C\mathit{H_2}CH_2$), 2.29 (m, 2H, $CF_2CH_2$), 3.47 (t, 2H, *J* 6.0 Hz, $CH_2Br$). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 24.1 ($CH_2\mathit{C}H_2CH_2$), 30.2 (t, *J* 22.0 Hz, $CF_2\mathit{C}H_2$), 32.0 ($CH_2Br$). Anal. Calcd for $C_{11}H_6BrF_{17}$: C, 24.42; H, 1.12; Br, 14.77; F, 59.69. Found: C, 23.92; H, 1.08; Br, 14.15; F, 59.53.

**3,5-(Di-3-(perfluorooctyl)propyloxy)benzyl Alcohol (2).** A mixture of **1** (45.0 g, 83.2 mmol), 3,5-dihydroxybenzyl alcohol (5.52 g, 39.4 mmol), $K_2CO_3$ (13.8 g, 100.2 mmol), and 18-crown-6 (2.10 g, 7.94 mmol) in dry acetone (200 mL) was heated under a nitrogen atmosphere. The reaction mixture was stirred vigorously with a magnetic stirrer and refluxed for 24 h. The mixture was dried on a rotary evaporator and partitioned between EtOAc and $H_2O$. The organic layer was washed two more times with $H_2O$ and dried over $MgSO_4$. After filtration and removal of solvent, the crude product was recrystallized from a small amount of $Et_2O$ to afford the product **2** as a white powder (30.4 g, 73.1%); mp 83−84 °C. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 1.56 (s, 1H, OH), 2.10 (m, 4H, $CH_2C\mathit{H_2}CH_2$), 2.31 (m, 4H, $CH_2CF_2$), 4.03 (t, 4H, *J* 6.0 Hz, $CH_2O$), 4.64 (s, 2H, $C\mathit{H_2}OH$), 6.37 (t, 1H, *J* 2.0 Hz, ArH), 6.53 (d, 2H, *J* 2.0 Hz, ArH). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$, ppm): 20.8 (2C, $CH_2\mathit{C}H_2CH_2$), 28.2 (t, 2C, *J* 22.5 Hz, $CF_2\mathit{C}H_2$), 65.5 (1C, $CH_2OH$), 66.6 (2C, $CH_2O$), 100.9 (1C, ArCH), 105.6 (2C, ArCH), 143.8 (1C, Ar$\mathit{C}CH_2OH$), 160.3 (2C, ArCO). Anal. Calcd for $C_{29}H_{18}F_{34}O_3$: C, 32.85; H, 1.71; F, 60.91. Found: C, 32.58; H, 1.68; F, 60.08.

**3,5-(Di-3-(perfluorooctyl)propyloxy)benzyl Bromide, Initiator A1.** Compound **2** (14.0 g, 13.2 mmol) was dissolved in dry THF (100 mL) in a two-necked round-bottomed flask equipped with a magnetic stirrer and $N_2$ inlet. $CBr_4$ (8.70 g, 26.2 mmol) was added to the solution, followed by $PPh_3$ (5.95 g, 22.7 mmol) which was added in four aliquots over 3 h. The reaction was left for a total of 6 h and quenched by addition of a small amount of $H_2O$. The mixture was dried on a rotary evaporator and partitioned between $CH_2Cl_2$ and $H_2O$. The organic layer was washed two more times with $H_2O$ and dried over $MgSO_4$. After filtration and removal of solvent, the crude product was recrystallized from 4:1 EtOAc/MeOH to afford the product, A1, as a fine white powder (11.9 g, 80.4%); mp 63−64 °C. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.10 (m, 4H, $CH_2C\mathit{H_2}CH_2$), 2.30 (m, 4H, $CH_2CF_2$), 4.02 (t, 4H, *J* 6.0 Hz, $CH_2O$), 4.41 (s, 2H, $CH_2Br$), 6.38 (t, 1H, *J* 2.0 Hz, ArH), 6.54 (d, 2H, *J* 2.0 Hz, ArH). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 20.9 (2C, $CH_2\mathit{C}H_2CH_2$), 28.3 (t, 2C, *J* 22.0 Hz, $CF_2\mathit{C}H_2$), 33.6 (1C, $CH_2Br$), 66.8 (2C, $CH_2O$), 101.9 (1C, ArCH), 108.2 (2C, ArCH), 140.4 (1C, Ar$\mathit{C}CH_2Br$), 160.3 (2C, ArCO). Anal. Calcd for $C_{29}H_{17}BrF_{34}O_2$: C, 31.01; H, 1.53; Br, 7.11; F, 57.50. Found: C, 31.03; H, 1.50; Br, 6.97; F, 57.32.

**3,5-(Di-3-(perfluorooctyl)propyloxy)benzyl-2-bromo-2-methylpropanoate, Initiator A2.** Compound **2** (2.00 g, 1.89 mmol) was dissolved in dry THF (30 mL), and dried triethylamine (0.29 mL, 2.08 mmol) was added to the solution. 2-Bromo-2-methyl propionyl bromide (0.25 mL, 2.02 mmol) was added dropwise to the mixture with stirring. The mixture was allowed to react at ambient temperature for 24 h. The product was isolated by filtering off the salt formed and evaporating the solvent. The latter was dissolved in $CH_2Cl_2$ and washed twice with saturated $NaHCO_3$ solution followed by two $H_2O$ washes. The organic layer was separated and dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude product was recrystallized from hexane to afford the product A2 as fine white crystals (1.75 g, 76.8%); mp 59−60 °C. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 1.96 (s, 6H, $C(CH_3)_2$), 2.05 (m, 4H, $CH_2C\mathit{H_2}CH_2$), 2.28 (m, 4H, $CH_2CF_2$), 4.03 (t, 4H, *J* 6.0 Hz, $CH_2C\mathit{H_2}O$), 5.15 (s, 2H, $CH_2OCO$), 6.41 (t, 1H, *J* 2.0 Hz, ArH), 6.53 (d, 2H, *J* 2.0 Hz, ArH). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 20.9 (2C, $CH_2\mathit{C}H_2CH_2$), 28.4 (t, 2C, *J* 22.0 Hz, $CF_2\mathit{C}H_2$), 31.2 (2C, $C(\mathit{C}H_3)_2$), 56.1 (1C, $\mathit{C}(CH_3)_2$), 66.9 (2C, $CH_2\mathit{C}H_2O$), 67.6 (1C, $\mathit{C}H_2OCO$), 101.8 (1C, ArCH), 106.7 (2C, ArCH), 138.4 (1C, Ar$\mathit{C}CH_2O$), 160.3 (2C, ArCO), 171.8 (1C, $CH_2O\mathit{C}O$). Anal. Calcd for $C_{33}H_{23}BrF_{34}O_4$: C, 32.77; H, 1.92; Br, 6.61; F, 53.41. Found: C, 32.80; H, 1.88; Br, 6.68; F, 52.75.

**Methyl 3,4,5(Tri-3-(perfluorooctyl)propyloxy)benzoate (3).** Compound **3** was prepared from a mixture of **1** (10.0 g, 18.5 mmol), methyl 3,4,5-trihydroxybenzoate (1.08 g, 5.89 mmol), $K_2CO_3$ (3.10 g, 22.4 mmol), and 18-crown-6 (0.469 g, 1.77 mmol) in dry acetone

(30 mL) by following the procedure used for compound **2**. The reaction mixture was worked up as in **2**, and the crude product was recrystallized from acetone to afford the product **3** as white crystals (6.81 g, 73.8%); mp 87−88 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.04 (m, 2H, $CH_2CH_2CH_2$), 2.14 (m, 4H, $CH_2CH_2CH_2$), 2.32 (m, 6H, $CH_2CF_2$), 3.91 (s, 3H, $OCH_3$), 4.06 (t, 2H, *J* 6.0 Hz, $CH_2O$), 4.12 (t, 4H, *J* 6.0 Hz, $CH_2O$), 7.28 (s, 2H, ArH). $^{13}$C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.9 (2C, $CH_2CH_2CH_2$), 21.8 (1C, $CH_2CH_2CH_2$), 28.2 (t, 3C, *J* 22.0 Hz, $CF_2CH_2$), 52.7 (1C, $OCH_3$), 67.9 (2C, $CH_2CH_2O$), 72.2 (1C, $CH_2CH_2O$), 108.6 (2C, ArCH), 126.0 (1C, ArCCOO), 141.8 (1C, ArCO), 152.5 (2C, ArCO), 166.8 (1C, COO). Anal. Calcd for $C_{41}H_{23}F_{51}O_5$: C, 31.48; H, 1.48; F, 61.93. Found: C, 31.23; H, 1.44; F, 60.65.

**3,4,5(Tri-3-(perfluorooctyl)propyloxy)benzyl Alcohol (4)** A solution of **3** (3.00 g, 1.92 mmol) in dry THF (40 mL) was added dropwise to a suspension of lithium aluminum hydride (0.100 g, 2.60 mmol) in THF (2.6 mL). The mixture was refluxed under a $N_2$ atmosphere for 1 h and left to cool, and NaOH (1 M, 2 mL) was added. The mixture was filtered, evaporated to dryness, and passed over a silica gel column using EtOAc as eluent. Compound **4** was recrystallized from acetone to give white crystals (2.51 g, 85.1%); mp 79−81 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.66 (s, 1H, OH), 2.01 (m, 2H, $CH_2CH_2CH_2$), 2.11 (m, 4H, $CH_2CH_2CH_2$), 2.30 (m, 6H, $CH_2CF_2$), 3.98 (t, 2H, *J* 6.0 Hz, $CH_2O$), 4.08 (t, 4H, *J* 6.0 Hz, $CH_2O$), 4.62 (s, 2H, $CH_2OH$), 6.60 (s, 2H, ArH). $^{13}$C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.7 (2C, $CH_2CH_2CH_2$), 21.5 (1C, $CH_2CH_2CH_2$), 28.0 (t, 3C, *J* 22.0 Hz, $CF_2CH_2$), 65.3 (1C, $CH_2OH$), 67.6 (2C, $CH_2CH_2O$), 71.8 (1C, $CH_2CH_2O$), 105.6 (2C, ArCH), 133.4 (1C, $ArCCH_2OH$), 139.2 (1C, ArCO), 152.6 (2C, ArCO). Anal. Calcd for $C_{40}H_{23}F_{51}O_4$: C, 31.27; H, 1.51; F, 63.06. Found: C, 31.00; H, 1.43; F, 62.38.

**3,4,5-(Tri-3-(perfluorooctyl) propyloxy)benzyl-2-bromo-2-methylpropanoate, Initiator B1.** Initiator B1 was prepared from **4** (1.50 g, 0.977 mmol), triethylamine (0.17 mL, 1.22 mmol), and 2-bromoisobutyryl bromide (0.15 mL, 1.22 mmol) in dry THF (20 mL) by following the procedure used for initiator A2. The reaction was left for 35 h, and the mixture was worked up as in A2, except that EtOAc was used instead of $CH_2Cl_2$ as solvent. The crude product was recrystallized from $CH_2Cl_2$ to afford B1 as a white powder (1.25 g, 75.8%); mp 85−86 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.96 (s, 6H, $C(CH_3)_2$), 2.02 (m, 2H, $CH_2CH_2CH_2$), 2.12 (m, 4H, $CH_2CH_2CH_2$), 2.32 (m, 6H, $CH_2CF_2$), 3.99 (t, 2H, *J* 6.0 Hz, $CH_2O$), 4.07 (t, 4H, *J* 6.0 Hz, $CH_2O$), 5.13 (s, 2H, $CH_2OCO$), 6.60 (s, 2H, ArH). $^{13}$C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.7 (2C, $CH_2CH_2CH_2$), 21.4 (1C, $CH_2CH_2CH_2$), 28.1 (t, 3C, *J* 22.0 Hz, $CF_2CH_2$), 30.7 (2C, $C(CH_3)_2$), 55.8 (1C, $C(CH_3)_2$), 67.2 (2C, $CH_2CH_2O$), 67.6 (1C, $CH_2OCO$), 71.8 (1C, $CH_2CH_2O$), 106.6 (2C, ArCH), 131.6 (1C, $ArCCH_2O$), 137.5 (1C, ArCO), 152.6 (2C, ArCO), 171.3 (1C, $CH_2OCO$). Anal. Calcd for $C_{44}H_{28}F_{51}O_5$: C, 31.35; H, 1.67; Br 4.74; F, 57.48. Found: C, 31.20; H, 1.65; Br, 3.68; F, 53.62.

**$(C_8F_{17}(CH_2)_3O)_4$-[G-1]-OH (5).** Compound **5** was prepared from a mixture of initiator A1 (7.60 g, 6.77 mmol), 3,5-dihydroxybenzyl alcohol (0.462 g, 3.30 mmol), $K_2CO_3$ (1.46 g, 10.6 mmol), and 18-crown-6 (0.080 g, 0.303 mmol) in dry acetone (20 mL) by following the procedure used for compound **2**. The reaction mixture was worked up as in **2**, and the crude product was purified by column chromatography eluting with pure $CH_2Cl_2$, gradually changing to pure EtOAc to give **5** as a white powder (6.10 g, 83.2%); mp 97−98 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.55 (s, 1H, OH), 2.09 (m, 8H, $CH_2CH_2CH_2$), 2.25 (m, 8H, $CH_2CF_2$), 4.03 (t, 8H, *J* 5.6 Hz, $CH_2CH_2O$), 4.64 (s, 2H, $CH_2OH$), 4.97 (s, 4H, $CCH_2O$), 6.39 (t, 2H, *J* 2.0 Hz, $Ar_2H$), 6.51 (t, 1H, *J* 2.4 Hz, $Ar_1H$), 6.57 (d, 4H, *J* 2.0 Hz, $Ar_2H$), 6.61 (d, 2H, *J* 2.4 Hz, $Ar_1H$). $^{13}$C NMR (125 MHz, $CDCl_3$, δ, ppm): 20.9 (4C, $CH_2CH_2CH_2$), 28.3 (t, 4C, *J* 22.5 Hz, $CF_2CH_2$), 65.6 (1C, $CH_2OH$), 66.8 (4C, $CH_2CH_2O$), 70.2 (2C, $CCH_2O$), 101.2 (2C, $Ar_2CH$), 101.7 (1C, $Ar_1CH$), 106.1 (2C, $Ar_1CH$), 106.3 (4C, $Ar_2CH$), 139.8 (2C, $Ar_2CCH_2O$), 143.8 (1C, $Ar_1CCH_2OH$), 160.3 (4C, $Ar_2CO$), 160.4 (2C, $Ar_1CO$). Anal. Calcd for $C_{65}H_{40}F_{68}O_7$: C, 35.09; H, 1.81; F, 58.06. Found: C, 34.99; H, 1.79; F, 57.79.

**$(C_8F_{17}(CH_2)_3O)_4$-[G-1]-Br, Initiator C1.** C1 was prepared from **5** (1.50 g, 0.674 mmol), $CBr_4$ (0.448 g, 1.35 mmol), and $PPh_3$ (0.320 g, 1.22 mmol) in dry THF (20 mL) by following the procedure used for compound A1. The reaction was left for 14 h, and the mixture was worked up as in A1, except that EtOAc was used instead of $CH_2Cl_2$ as solvent. The crude product was recrystallized from $CH_2Cl_2$ to afford C1 as a white powder (1.10 g, 71.4%); mp 87−89 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.10 (m, 8H, $CH_2CH_2CH_2$), 2.31 (m, 8H, $CH_2CF_2$), 4.04 (t, 8H, *J* 5.8 Hz, $CH_2CH_2O$), 4.47 (s, 2H, $CH_2Br$), 4.97 (s, 4H, $CCH_2O$), 6.41 (t, 2H, *J* 2.0 Hz, $Ar_2H$), 6.53 (t, 1H, *J* 2.0 Hz, $Ar_1H$), 6.58 (d, 4H, *J* 2.0 Hz, $Ar_2H$), 6.64 (d, 2H, *J* 2.0 Hz, $Ar_1H$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.8 (4C, $CH_2CH_2CH_2$), 28.2 (t, 4C, *J* 22.0 Hz, $CF_2CH_2$), 33.7 (1C, $CH_2Br$), 66.7 (4C, $CH_2CH_2O$), 70.2 (2C, $CCH_2O$), 101.3 (2C, $Ar_2CH$), 102.5 (1C, $Ar_1CH$), 106.3 (4C, $Ar_2CH$), 108.5 (2C, $Ar_1CH$), 139.5 (2C, $Ar_2CCH_2O$), 140.3 (1C, $Ar_1CCH_2Br$), 160.2 (2C, $Ar_1CO$), 160.3 (4C, $Ar_2CO$). Anal. Calcd for $C_{65}H_{39}BrF_{68}O_6$: C, 34.13; H, 1.72; Br, 3.49; F, 56.47. Found: C, 34.07; H, 1.71; Br, 3.22; F, 56.69.

**$(C_8F_{17}(CH_2)_3O)_4$-[G-1]-$OCOC(CH_3)_2Br$, Initiator C2.** C2 was prepared from **5** (2.00 g, 0.899 mmol), triethylamine (0.14 mL, 0.992 mmol), and 2-bromo-2-methylpropionyl bromide (0.12 mL, 0.992 mmol) in dry THF (30 mL) by following the procedure used for initiator A2. The reaction was left for 40 h, and the mixture was worked up as in A2, except that EtOAc was used instead of $CH_2Cl_2$ as solvent. The crude product was recrystallized from $CH_2Cl_2$ to afford C2 as a white powder (1.34 g, 62.9%); mp 85−86 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.09 (m, 8H, $CH_2CH_2CH_2$), 2.30 (m, 8H, $CH_2CF_2$), 4.02 (t, 8H, *J* 6.0 Hz, $CH_2CH_2O$), 4.97 (s, 4H, $CCH_2O$), 5.14 (s, 2H, $CH_2OCO$), 6.40 (t, 2H, *J* 2.0 Hz, $Ar_2H$), 6.54 (t, 1H, *J* 2.0 Hz, $Ar_1H$), 6.57 (d, 4H, *J* 2.0 Hz, $Ar_2H$), 6.60 (d, 2H, *J* 2.0 Hz, $Ar_1H$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.8 (4C, $CH_2CH_2CH_2$), 28.2 (t, 4C, *J* 22.0 Hz, $CF_2CH_2$), 31.0 (2C, $C(CH_3)_2$), 57.0 (1C, $C(CH_3)_2$), 66.7 (4C, $CH_2CH_2O$), 67.4 (1C, $CH_2OCO$), 70.2 (2C, $CCH_2O$), 101.2 (2C, $Ar_2CH$), 102.4 (1C, $Ar_1CH$), 106.2 (4C, $Ar_2CH$), 106.9 (2C, $Ar_1CH$), 138.2 (1C, $Ar_1CCH_2O$), 139.6 (2C, $Ar_2CCH_2O$), 160.2 (2C, $Ar_1CO$), 160.3 (4C, $Ar_2CO$), 172.0 (1C, $CH_2OCO$). Anal. Calcd for $C_{69}H_{45}BrF_{68}O_8$: C, 34.91; H, 1.91; Br, 3.37; F, 54.42. Found: C, 34.84; H, 1.81; Br, 3.37; F, 53.64.

**Copper-Mediated Living Radical Polymerizations.** Copper-mediated living radical polymerization was carried out under a nitrogen atmosphere using standard Schlenk techniques. An example of a styrene-$d_8$ polymerization is as follows: Cu(I)Br (0.036 g, 0.25 mmol), initiator A1 (0.281 g, 0.25 mmol), and 2,2′-dipyridyl (0.078 g, 0.50 mmol) were placed together with a magnetic stirrer bar in an oven-dried Schlenk tube. The tube was fitted with a rubber septum, evacuated, and filled with nitrogen three times. Deoxygenated styrene-$d_8$ (2.55 mL, 22.3 mmol) was transferred to the Schlenk tube via syringe. The mixture was further degassed by three freeze−pump−thaw cycles. The polymerization was carried out under a nitrogen atmosphere at 110 °C for ∼18 h. The reaction mixture was left to cool, diluted in toluene, and passed over an alumina column. The polymer solution was precipitated in methanol, collected by filtration, and dried under vacuum (yield ca. 2 g). $M_n = 10\,500$ g mol$^{-1}$, $M_w = 12\,900$ g mol$^{-1}$, $M_w/M_n = 1.23$.

The same procedure was employed for the polymerization of methyl methacrylate, except that *N*-(*n*-propyl)-2-pyridylmethanimine was used as the ligand ([ligand]/[Cu salt] = 2:1) and the reactions were carried out in toluene solution. Ligand and toluene were added at the same stage as monomer addition. Polymerizations were carried at 90 °C and were left for 5−11 h. Poly(methyl methacrylate) was collected by precipitation into hexane.

## Results and Discussion

The principal objective of this work was to develop a generic methodology to synthesize a series of polymer additives, which when added at low concentrations to a bulk polymer, would spontaneously migrate to the polymer−air surface whereupon the additives would modify the surface properties of the bulk

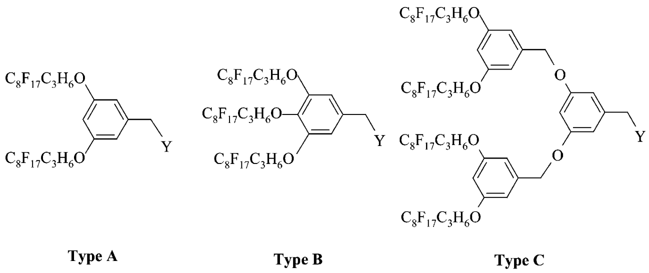
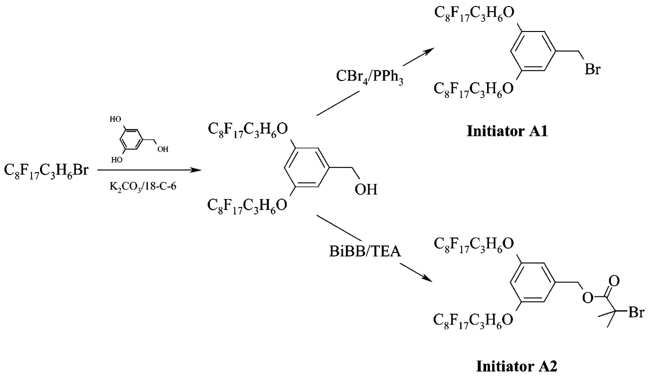


**Figure 2.** Controlled radical polymerization initiators carrying multiple fluoroalkyl groups.

**Scheme 1. Synthesis of Type A Initiators Bearing 2 CF Groups**



polymers. A series of initiators carrying multiple fluoroalkyl (CF) groups have been synthesized and used for the controlled radical polymerization of vinyl monomers, e.g., styrene (Sty) and methyl methacrylate (MMA), with a view to preparing polymer additives carrying multiple CF groups at one end. The two key structural parameters that will determine the effectiveness of these additives are the number of CF groups and the molecular weight of the polymer chain. Initiators carrying 2, 3, and 4 CF groups have been used in tandem with a living radical polymerization mechanism which offers the opportunity to control the molecular weight of the pendant polymer chain of the additive with the long-term aim being to optimize the surface modifying properties.

**Initiators.** Three groups of initiators have been prepared (see Figure 2): type A carrying 2 CF groups, type B carrying 3 CF groups, and type C carrying 4 CF groups. The exact nature of the initiating moiety Y varies depending on the polymerization in question, and one of the real advantages of the described strategy is that the nature of Y may be modified according to the polymer to be made. This flexibility also means that these molecules are not limited solely to use as initiators in free radical mechanisms. We have recently demonstrated that a type A initiator in which Y is a hydroxyl group can be used in the presence of stannous octoate for the ring-opening polymerization of lactide. The synthesis of a polylactide additive and a detailed discussion of its surface modifying properties are reported elsewhere.[54]

**Synthesis of Type A Initiators.** Type A initiators were made in two steps via the Williamson coupling reaction between 3-(perfluorooctyl)propyl bromide and 3,5-dihydroxybenzyl alcohol followed by conversion of the benzyl alcohol to the desired "Y" functionality according to Scheme 1. In the case of initiator A1 this involved conversion of the alcohol to a benzyl bromide moiety, and A2 was prepared by reaction of the alcohol with 2-bromoisobutyryl bromide (BiBB).

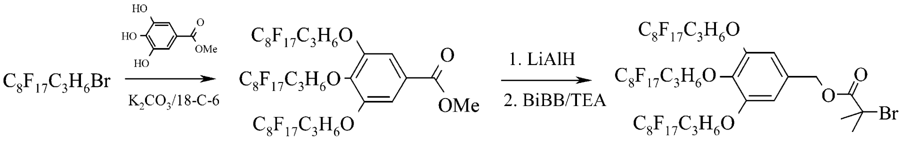
**Synthesis of Type B Initiator.** Initiator B1 was synthesized via the Williamson coupling of 3-(perfluorooctyl)propyl bromide to methyl 3,4,5-trihydroxybenzoate (methyl gallate) followed by hydrolysis of the ester functionality to a benzyl alcohol with lithium aluminum hydride. The final step involves the reaction of the alcohol with BiBB to yield the initiator according to Scheme 2.

**Synthesis of Type C Initiators.** Type C initiators are G1 dendrons and can be made in two steps from the G0 dendron (initiator A1). A Williamson coupling reaction between initiator A1 and 3,5-dihydroxybenzyl alcohol was followed by conversion of the benzyl alcohol into the desired functionality either by reaction with $CBr_4/PPh_3$ or BiBB according to Scheme 3 to yield initiators C1 and C2, respectively.

**Polymerizations.** Using each of these three types of initiator, a series of polymers have been prepared by copper-mediated controlled radical polymerization, also known as atom transfer radical polymerization (ATRP). ATRP as a mechanism offers a high degree of control over polymerization, resulting in polymers with predictable molecular weights and reasonably narrow molecular weight distributions ($M_w/M_n < 1.5$).[55−57] The use of Fréchet type benzyl aryl ether dendrons with a benzyl bromide core functionality as initiators for ATRP has been reported previously.[47] A third generation dendritic initiator was used to polymerize styrene with a variety of molecular weights, and we adopted this approach which uses a Cu(I)Br/2,2′-dipyridyl catalytic system for the bulk polymerization of styrene at 110 °C using the synthesized initiators bearing multiple fluoroalkyl groups. Initiators A1, B1, and C1 were successfully used to prepare several samples of polystyrene. The molecular weights and polydispersity values for each of the polystyrenes prepared are given in Table 1. It should be noted that in all cases perdeuterated styrene was used as the monomer in these polymerizations, deuterated polymers being required to facilitate subsequent characterization studies by ion beam analysis, neutron reflectometry, and small-angle neutron scattering. These characterization techniques allow a detailed study of the physical properties of the end-capped polymers that are important to their function as additives. Small-angle neutron scattering provides evidence of aggregation in bulk, which can be a significant limiting factor in the effectiveness of block copolymer additives.[58] Ion beam analysis quantifies the rates of interdiffusion of these additives with the corresponding bulk homopolymer as well as the surface excess of adsorbed material. Neutron reflectometry can resolve the detailed structure of the adsorbed layer, allowing comparison with self-consistent mean-field theory models of adsorption, and the extent of mixing between adsorbed polymer chains and the bulk material immediately adjacent to the surface. A full discussion of the results of these studies will be reported in a forthcoming publication.

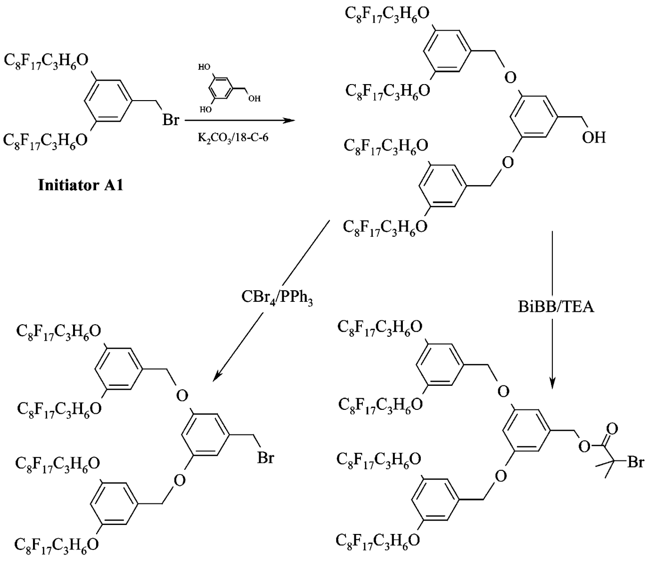
Although we are confident that the molecular weight data obtained by SEC are sufficiently accurate to draw reliable conclusions, we acknowledge the use of such bulky initiators presents certain issues that we should recognize. In both Table 1 (polystyrene samples) and Table 2 (PMMA samples, below) the target molecular weights quoted are for the resulting polymer chain (assuming 100% conversion), excluding the molecular weight of the initiator residue. However, one might reasonably expect that the end group introduced from the initiator would contribute to the molecular weight obtained by SEC. In the case of the type A initiators the end group has a molar mass of 1043; in the case of type B and C this increases to 1519 and 2175, respectively. While it is not easy to accurately determine what contribution the end group makes to the hydrodynamic volume of the polymers during SEC analysis, we can be sure that any error associated with the molecular weights will becoming smaller as the molecular weight of the polymer sample increases.

**Scheme 2. Synthesis of Type B Initiator Bearing 3 CF Groups**



**Initiator B1**

**Scheme 3. Synthesis of Type C Initiators Bearing 4 CF Groups**



**Initiator C1** **Initiator C2**

It should also be noted that where comparisons were made between the value of $M_n$ obtained by SEC and $^1$H NMR for PMMA (see Table 2), the two values were in very good agreement.

It can be seen from the data in Table 1 that the use of initiator A1 for ATRP of styrene results in polymers which have molecular weights (by SEC) that are in reasonable agreement with expectation and values of $M_w/M_n$ between 1.15 and 1.26, implying good control over a range of molecular weights. An initial attempt to use B1 was prematurely quenched, resulting in a lower molecular weight than intended, but when the experiment was repeated according to the correct protocol, the polymerization resulted in a molecular weight in good agreement with expectation and a polydispersity index of 1.33. ATRP of styrene with initiator C1, with four CF groups, however, only appears to offer good control at lower molecular weights. When attempting to prepare a polymer with a molecular weight ($M_n$) of 30 000 g mol$^{-1}$, conversion of monomer and therefore yields were modest, and the resulting polymer had a molecular weight slightly less than half of that expected from the stoichiometric ratio of monomer to initiator.

Initial attempts to polymerize PMMA using initiators with a benzyl bromide functionality were less successful. Using initiator A1, we were able to polymerize methyl methacrylate (MMA) (using Cu(I)Cl/*N*-(*n*-propyl)-2-pyridylmethanimine as the catalyst combination and toluene as a solvent), but initiator efficiency was poor. A molecular weight of 30 000 g mol$^{-1}$ and PDI of 1.34 were obtained for a polymer with a calculated molecular weight of 10 000 g mol$^{-1}$ (see Table 2). This lack of control is maybe not surprising given that the benzyl bromide moiety is not ideal for the initiation of (meth)acrylates via ATRP. However, the use of initiators (A2, B1, and C2) functionalized with a bromoester moiety would be expected to be more suitable for the polymerization of MMA, and it proved to be the case.

It can be deduced from the data in Table 2 that A2, B1, and C2 are far more efficient initiators for ATRP of PMMA than A1 was. Molecular weights are in good agreement with expectation, and the values of $M_w/M_n$ are all less than 1.2. However, it should be noted that when initiator C2 (with 4 CF groups) was used, the $M_n$ obtained by SEC (and NMR) is somewhat lower than in the other two cases. Initiator C1 (with 4 CF groups) used for the polymerization of styrene similarly resulted in molecular weights which were lower than expected. To try and understand this behavior, we can refer to the kinetic plots and $M_n$ vs conversion plots for the polymerization of MMA.

We can see from Figure 3 that the polymerization of MMA, initiated by each of the three fluoroalkyl-functionalized initiators, proceeds through approximately first-order kinetics with respect to monomer concentration in the early stages of propagation (up to 5−6 h), at which point the rate of propagation begins to tail off. For comparison purposes we have included the data for the polymerization of MMA under the same conditions using ethyl 2-bromoisobutyrate (EBiB) as the initiator. For the first 5−6 h polymerizations initiated with A2, B1, and EBiB proceed at almost identical rates, whereas the polymerization initiated with C2 proceeds at a much slower rate. The deviation from first-order kinetics after 6 h is probably the result of some termination process, a process which appears to be more prevalent when using initiators A2 and C2. Why B1 initiator should show a more controlled polymerization than A2 or C2 is not clear. All the three initiators, A2, B1, and C2, are bromoesters, but polymerization using B1 was as controlled as that using the highly efficient ethyl 2-bromoisobutyrate, while polymerizations using A2 and in particular C2 showed nonideal behavior. The lower rate of propagation coupled with the apparent termination explains the poorer yields and lower molecular weights obtained when using C2, and one expects that similar behavior would explain the results obtained when using C1 for the polymerization of styrene.

$M_n$ increases almost linearly with conversion (Figure 4) for polymerizations initiated with each of the three types of fluoroalkyl initiator. In the case of A2 and B1 the relationship between $M_n$ and conversion is maintained up to ~80% conversion; however, in the case of C2 $M_n$ does not continue to evolve much above 50% conversion. In each case the molecular weight obtained by SEC is slightly higher than the theoretical value, which includes the molecular mass of the initiator.

**Contact Angle Measurements.** Contact angle measurements are a convenient method for obtaining information about the surface characteristics of a material and, in this case, the surface property modifying ability of the additives end-capped with 2, 3, or 4 CF groups. Measurements were carried out on films containing various concentrations of additives with both water and dodecane as the contact fluids. In this way we can investigate both the hydrophobicity and oleophobicity of the polymer film surfaces.

**Table 1. Molecular Weight and Polydispersity Index Data for a Series of Polystyrene Polymers Prepared by ATRP Using Fluoroalkyl Functionalized Initiators**

| initiator | target $M_n$/ g mol$^{-1}$ | $M_n$(SEC)$^a$/ g mol$^{-1}$ | $M_w$(SEC)/ g mol$^{-1}$ | $M_w/M_n$ |
|---|---|---|---|---|
| A1 | 10 000 | 10 500 | 12 900 | 1.23 |
| A1 | 15 000 | 15 100 | 19 000 | 1.26 |
| A1 | 35 000 | 28 000 | 32 200 | 1.15 |
| B1 | 10 000 | 5 500 | 7 000 | 1.28 |
| B1 | 10 000 | 11 200 | 14 900 | 1.33 |
| C1 | 10 000 | 10 200 | 12 300 | 1.21 |
| C1 | 20 000 | 15 000 | 18 600 | 1.24 |
| C1 | 30 000 | 14 000 | 20 000 | 1.43 |

[a] SEC data obtained using conventional calibration generated with a series of polystyrene standards.

**Polystyrene Additives.** Contact angle measurements were carried out on thin films of bulk polystyrene ($M_n = 250\,000$ g mol$^{-1}$, $M_w/M_n = 1.05$) containing various concentrations by weight of surface modifying additive. The data reported in Figure 4 are for A1(2CF)10K, a polystyrene additive ($M_n = 10\,500$, $M_w/M_n = 1.23$) initiated with A1 and therefore carrying 2 CF groups, B1(3CF)10K, a polystyrene additive ($M_n = 11\,200$, $M_w/M_n = 1.33$) initiated with B1 and carrying 3 CF groups, and C1(4CF)10K, a polystyrene additive ($M_n = 10\,200$, $M_w/M_n = 1.21$) initiated with C1 and 4 CF groups. Contact angles were measured on both "as-spun" dried films and films that had been annealed for 1 h at 160 °C.

The contact angle of unmodified polystyrene was measured to be ~90°, and it can be seen in Figure 5 that the addition of even very small quantities (1%) of additive results in a measurable increase in the contact angle. Increasing amounts of A1(2CF)10K results in a steady increase in the contact angle until a plateau is reached at about 100°, corresponding to ~10 wt % additive. Annealing the films for 1 h at 160 °C, well above the glass transition ($T_g$) of polystyrene, allows the films to reorganize. Contact angle measurements of the annealed films are generally slightly higher than the as-spun films. Although the data in Figure 5 are the average of three measurements, the differences may be too small to be statistically significant. One might tentatively argue that annealing has allowed more of the additive to segregate to the surface; however, annealing can also lead to a lowering of surface roughness which can similarly alter contact angles. Addition of B1(3CF)10K results in much more significant increases in contact angles. As little as 2% of this additive is enough to cause a 10−12° increase in contact angle over unmodified polystyrene. As with A1(2CF)10K a plateau in contact angle is reached at about 10 wt % B1(3CF)10K with a maximum contact angle of 107°. Once again there appears to be a benefit to annealing, which increases contact angles by 3−4°. While increasing the number of CF groups from 2 to 3 results in a significant improvement in surface properties, increasing the number of CF groups from 3 to 4 has a less pronounced effect. Qualitatively, the addition of C1(4CF)10K modifies the bulk polystyrene in a similar fashion to B1(3CF)10K. Contact angles rise steeply with increasing concentration of additive; at low concentrations (0−5%) the contact angles of B1(3CF)10K and C1(4CF)10K are nearly identical. Similarly to the other two additives C1(4CF)10K reaches a maximum in a contact angle at about 10 wt % of additive with a maximum contact angle of 110°. The only observation that can be made about the difference between B1(3CF)10K and C1(4CF)10K is that while in the former case annealing appears to result in a small (3−4°) but consistent increase in contact angle, in the latter case the differences between annealed and as-spun films are less pronounced and too small to indicate any clear benefit to annealing. In summary, we can see that each of these additives is surface active enough to segregate to the air polymer interface during the lifetime of the spin-coating process and to significantly modify the surface properties of the resulting films. In the case of A1(2CF)10K and B1(3CF)10K annealing for 1 h at 160 °C appears to result in slightly higher contact angles, which we believe is consistent with enhanced surface segregation. The higher fluorine content of C1(4CF)10K seems to enhance surface segregation during the spin-coating process such that annealing has a less pronounced effect. Only at the lowest concentration of this additive (1%) is there a significant increase in contact angle due to annealing, the angle rising from 93° to 97°. The maximum contact angles attained by the addition of additives B1(3CF)10K (111° after annealing) and C1(4CF)10K (110°) compare very favorably with the contact angle of water on pure polytetrafluoroethylene (PTFE), which has been quoted as 108°.[59,60] The formation of a plateau/maximum in contact angle at about 10 wt % for all three additives suggests that saturation of the surface with additive molecules has occurred, and clearly the addition of further amounts of additive does little to further modify the surface. As all three additives have polymer chains of near identical molecular weight, it is not surprising that surface saturation is observed at similar concentrations of additive as it is certain that the concentration of additive molecules at a surface will be determined by the molecular weight and therefore radius of gyration of the pendant polymer chain rather than size of the head group at the surface.

Similar behavior is observed for contact angles measured with dodecane as the contact fluid (Figure 6). Dodecane completely wets unmodified polystyrene, and no measurable contact angle results. However, the addition of as little as 1% of either A1(2CF)10K or C1(4CF)10K results in a measurable increase in

**Table 2. Molecular Weight and Polydispersity Index Data for a Series of PMMA Polymers Prepared by ATRP Using Fluoroalkyl-Functionalized Initiators**

| initiator | target $M_n$/ g mol$^{-1}$ | $M_n$(SEC)$^c$/ g mol$^{-1}$ | $M_w$(SEC)/ g mol$^{-1}$ | $M_n$(NMR)/ g mol$^{-1}$ | $M_w$/ $M_n$ |
|---|---|---|---|---|---|
| A1$^a$ | 10 000 | 29 200 | 39 100 |  | 1.34 |
| A2$^b$ | 10 000 | 10 900 | 13 000 | 10 400 | 1.19 |
| B1$^b$ | 10 000 | 9 900 | 11 200 | 11 200 | 1.13 |
| C2$^b$ | 10 000 | 7 200 | 8 300 | 7 500 | 1.15 |

[a] Cu(I)Cl/*N*-(*n*-propyl)-2-pyridylmethanimine in toluene. [b] Cu(I)Br/*N*-(*n*-propyl)-2-pyridylmethanimine in toluene. [c] SEC relative to PMMA standards.

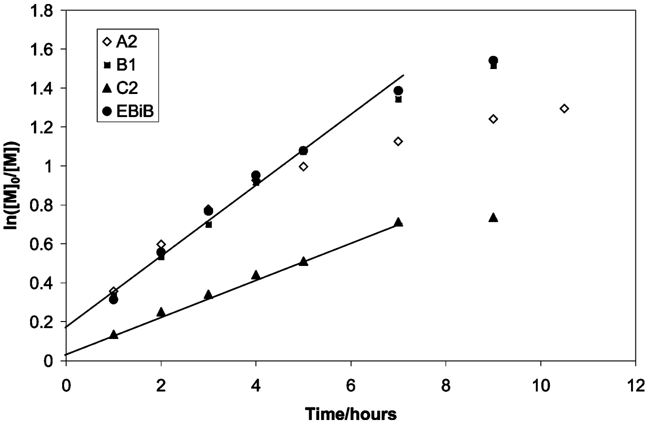


**Figure 3.** Kinetic plots for the polymerization of methyl methacrylate with initiators A2, B1, C2, and ethyl 2-bromoisobutyrate (EBiB) in toluene at 90 °C. [MMA]/[CuBr]/[*N*-(*n*-propyl)-2-pyridylmethanimine]/[initiator] = 100/1/2/1.

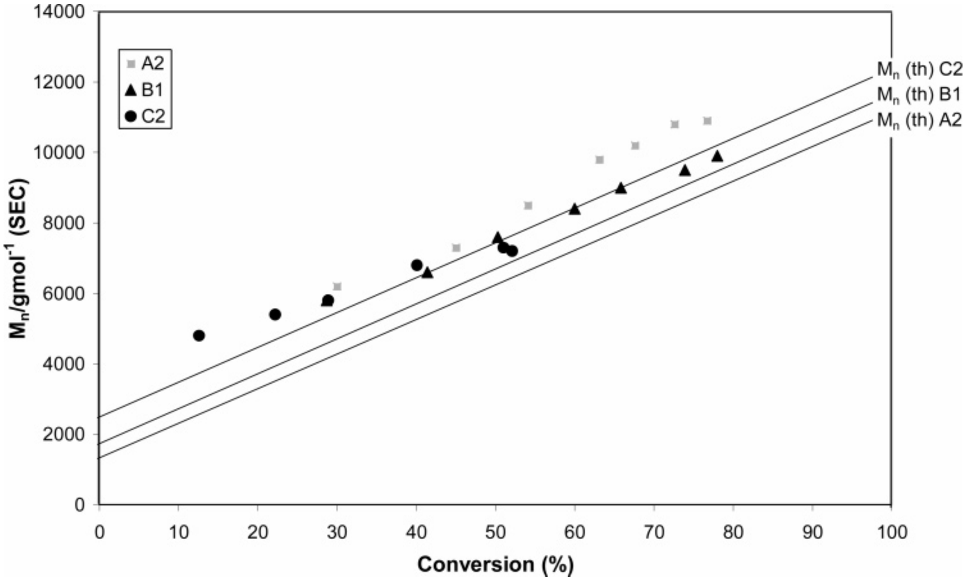


**Figure 4.** Evolution of $M_n$ with conversion of monomer for the polymerization of MMA with initiators A2, B1, and C2 in toluene at 90 °C. [MMA]/[CuBr]/[*N*-(*n*-propyl)-2-pyridylmethanimine]/[initiator] = 100/1/2/1.

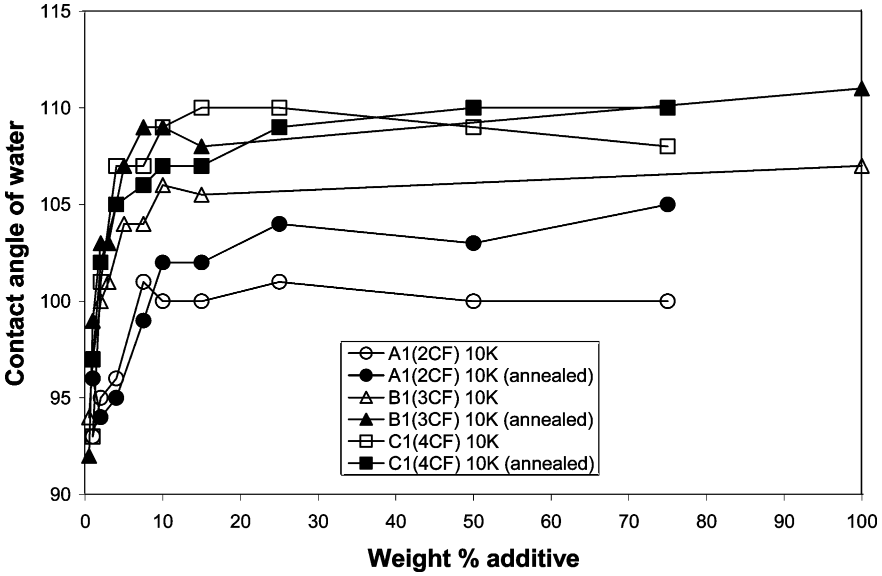


**Figure 5.** Contact angle of water on polystyrene film vs concentration of additive for three polystyrene additives A1(2CF)10K, B1(3CF)10K, and C1(4CF)10K, $M_n$ ~10 000 g mol$^{-1}$, end-functionalized with 2, 3, and 4 fluoroalkyl groups, respectively.

the oleophobicity of the surface and a contact angle of ~20°. Increasing amounts of A1(2CF)10K results in increasing contact angles up to a maximum of 32° for the as-spun films and 35° for the annealed films. Addition of C1(4CF)10K leads to a far more striking increase in contact angles. A plateau in contact angle with dodecane (as with water) is observed after the addition of ~10 wt % of additive C1(4CF)10K with a maximum of a little under 60° for the as-spun films and a little over 60° for the annealed films. The use of dodecane as a contact fluid appears to be a more sensitive test of the effect of annealing. Although the increase in contact angle due to annealing does show some inconsistency, for example, the increase seen for the 10% blend of A1(2CF)10K is anomalously low, but for both additives and at every concentration there is an increase in contact angle after annealing. In the case of C1(4CF)10K at the lowest concentration (1%) the increase in contact angle with dodecane after annealing is only 1°; however, it is likely that at this very low concentration the short annealing time (1 h) may not be sufficient to dramatically alter the surface segregation (see below discussion on effect of annealing time). However, at 2% of additive the increase in contact angle is 8°, and at for concentrations of 4%, 7.5%, and 10% the increase in contact angle due to annealing is 12°, 9°, and 13°, respectively. It is maybe not surprising that as the concentration of additive in the bulk increases above 10%, the kinetics of surface segregation improve dramatically due to the higher concentration, and the benefit of annealing falls away. The average increase in contact angle due to annealing for concentrations above 10% is less than 7°.

**Effect of Annealing Time on Surface Segregation**. To further investigate the effect of annealing on the surface segregation of fluoroalkyl end-functionalized additives a PS film containing 1 wt %, C1(4CF)10K was annealed at 160 °C for up to 12 h. It was postulated in the previous section that annealing such a film for 1 h may be insufficient to allow significantly enhanced surface segregation. Contact angle measurements of such a film with water as the contact fluid showed that annealing for 1 h resulted in a modest increase in

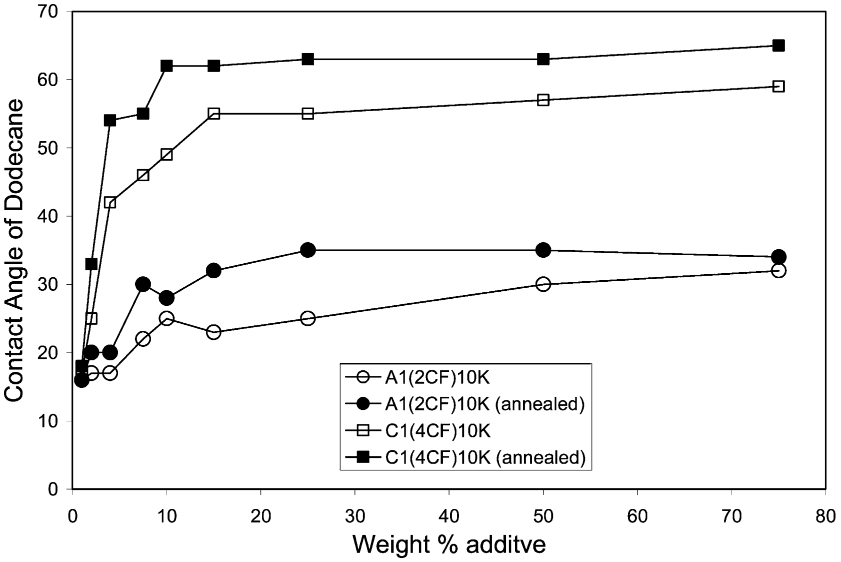


**Figure 6.** Contact angle of dodecane on polystyrene films vs concentration of additive for two polystyrene additives, A1(2CF)10K and C1(4CF)-10K, $M_n$ ~10 000 g mol$^{-1}$, end-functionalized with 2 and 4 fluoroalkyl groups, respectively.

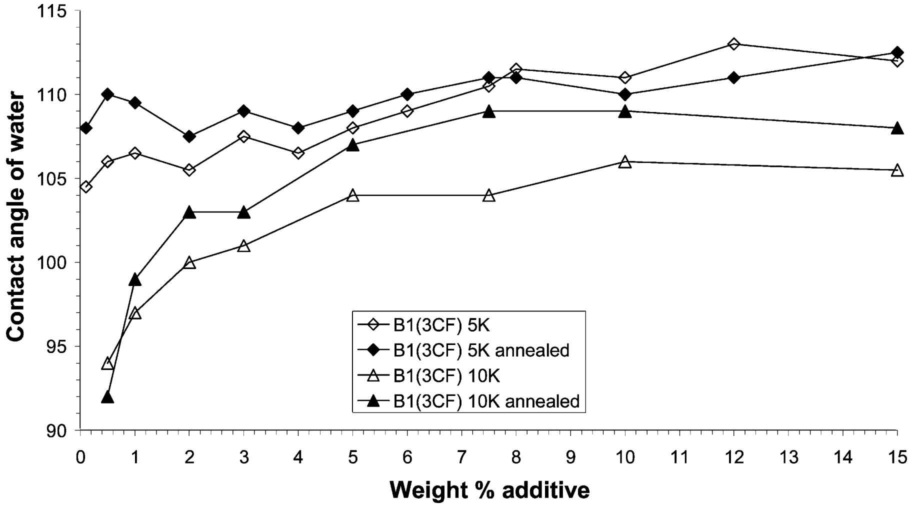


**Figure 7.** Contact angle of water on polystyrene film vs concentration of additive for two polystyrene additives of different molecular weight. B1(3CF)10K and B1(3CF)5K, each end-functionalized with three fluoroalkyl groups.

contact angle from 93° to 97°. However, annealing the film for a total of 12 h resulted in a significant increase in contact angle of 15° to 108°. This seems to confirm that at low concentrations of additive longer annealing times (or higher temperatures) are required to enhance surface segregation, but more noteworthy is the realization that concentrations of as little as 1% can, given prolonged annealing times, result in modified polymer surfaces with hydrophobicity approaching that of PTFE.

**Effect of Polystyrene Chain Length on Surface Segregation.** Kinetic and thermodynamic considerations suggest that molecular weight of the polymer additive would strongly influence surface segregation; a lower molecular weight would be expected to have an enhanced rate of diffusion through the matrix and therefore more rapidly surface segregate. Furthermore, since we expect that the maximum concentration of additive molecules at the surface to be determined by the molecular weight and therefore the radius of gyration of the pendant polymer chain rather than the size of the head group, we would expect a lower molecular weight additive would be able to more densely pack the surface with head groups and lead to enhanced surface properties. Figure 7 shows contact angle data for two additives both initiated with B1 and therefore carrying 3 CF groups. B1(3CF)10K has a molecular weight ($M_n$) of 11 200 g mol$^{-1}$, and B1(3CF)5K has a molecular weight ($M_n$) of 5500 g mol$^{-1}$. It can be seen that the lower molecular weight additive (B1(3CF)5K) shows remarkable surface activity such that even at the lowest concentration of additive (0.1 wt %) the as-spun film shows a contact angle of 104°. This is a vast improvement over B1(3CF)10K, which at 0.5% additive (as spun) has a contact angle of some 10° lower. As mentioned previously, it is at the lowest concentrations of additive when annealing appears to have the greatest effect. At concentrations of B1(3CF)5K of 1% and less, annealing for 1 h at 160° increases the contact angles by 3−4°; at higher concentrations annealing makes a far less obvious difference. We can also see from Figure 7 that not only is B1(3CF)5K able to dramatically alter the surface properties at significantly lower concentrations than B1(3CF)10K but that the maximum contact angle achieved with B1(3CF)5K is higher than that obtained with B1(3CF)-10K: 112−113° vs 108−109°. The increased surface activity at very low concentrations and higher maximum contact angle of B1(3CF)5K in comparison to B1(3CF)10K strongly supports the assertion that molecular weight of additive will strongly influence the rate of diffusion and therefore surface segregation and that the molecular weight of the pendant polymer chain of the additive will to a large extent dictate the concentration of functional head groups at the air−polymer surface and there control the degree to which the additive can modify surface properties.

**PMMA Additives.** Contact angle measurements on films prepared by the addition of PMMA additives carrying multiple fluoroalkyl end groups to bulk PMMA resulted in qualitatively similar behavior to polystyrene films. Increasing amounts of additive initially result in increasing contact angles up to approximately 10−15%, after which the rate of increase of contact angle with increasing contact angle decreased, suggesting the onset of surface saturation. Water has a contact angle of ∼67° on unmodified PMMA, whereas the measured contact angle for PMMA modified with an additive of molecular weight ($M_n$) 7200 g mol$^{-1}$ initiated by C2 and therefore carrying four CF groups (C2(4CF)7K PMMA) increased by 16° to 83° for a film containing 10% of additive (annealed for 1 h at 150 °C) and by a further 9° to 92° for an annealed film containing 15% C2(4CF)7K PMMA. Dodecane spreads on unmodified PMMA, resulting in an effective contact angle of 0°; however, addition of 10% C2(4CF)7K PMMA resulted in a contact angle of 31°, and 15% C2(4CF)7K PMMA gave a contact angle of 38°. Somewhat unexpectedly, an analogous PMMA additive carrying only 2 CF groups performed as well if not better than the 4CF additive. We suspect that a number of factors may have contributed to this behavior. The surface segregation of these polymer additives will depend to a large extent on their ability to diffuse through the bulk polymer to the surface. A key determinant of the rate of diffusion is how entangled the additive is with the bulk, and this in turn is dependent upon the molecular weight of the polymer expressed in terms of $nM_e$, where $M_e$ is the entanglement molecular weight. While surface segregation of the polystyrene samples appeared to be very rapid, it should be noted that $M_e$ of polystyrene[61] is ∼16 500 g mol$^{-1}$, and therefore the polystyrene additives with an $M_n$ of 10 000 g mol$^{-1}$ are only 0.6$M_e$. However, $M_e$ for PMMA is ∼4800 g mol$^{-1}$,[62] and therefore the PMMA additives with a molecular weight of ∼7000 g mol$^{-1}$ are almost 1.5$M_e$. The rates of polymer diffusion below and above $M_e$ are significantly different, and it is clear that this will play a key role in retarding surface segregation in the case of PMMA additives. A further consideration is the nature of the molecular structure. In the case of the C2(4CF)-7K PMMA additive the relatively short pendant chain, the higher degree of fluorination, and the obvious incompatibility of the two may lead to the onset of solid state organization, in the same way that block copolymers undergo microphase separation. Any self-organization into larger scale structures will also contribute to a reduction in the rate of surface segregation. Although there was no evidence from the contact angles to suggest that such behavior was inhibitive in the surface segregation of the polystyrene samples, RBS data on C1(4CF)-10K (see below) do imply that self-organization is a possibility. One final point is that the rate of diffusion during annealing will depend on temperature, and the polystyrene films were annealed for 1 h at 160 °C and the PMMA films for 1 h at 150 °C. While annealing the PMMA films for 1 h at 150 °C did result in modest increases in contact angles, it is likely that, as alluded to previously, more prolonged annealing may be required to approach surface saturation. Interestingly, the contact angle with water as the contact fluid on a film of pure C2-(4CF)7K PMMA was 111°, which implies that these PMMA additives are capable of significantly altering the surface properties of bulk PMMA to the same extent as the polystyrene additives, provided the additives have the correct structure and the films are appropriately treated.

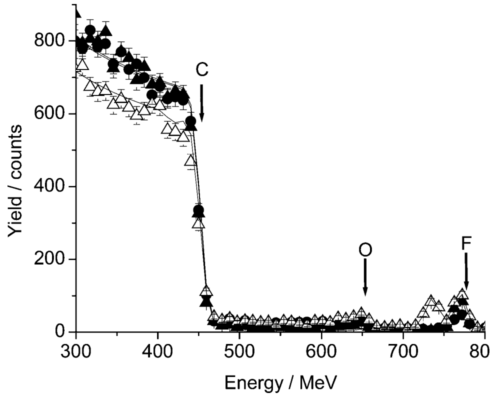


**Figure 8.** RBS data for films of polystyrene containing C1(4CF)10K at concentrations of 0.3% (filled circles), 1.0% (filled triangles), and 3% (open triangles). The elemental markers indicate the maximum recoil energy of $^4$He$^+$ from each element in the film surface.

**Ion Beam Analysis: Rutherford Back Scattering (RBS).** Although the static contact angle measurements clearly demonstrate (qualitatively) the effectiveness of these end-functionalized additives for modifying the surface properties and, furthermore, they reveal the influence of additive concentration, the number of fluoroalkyl groups, and the molecular weight of the pendant polymer chain on surface hydrophopbicity/oleophobicity, contact angle data cannot provide any quantitative information about the surface elemental composition. However, to quantify the near-surface concentration of fluorocarbon, Rutherford backscattering (RBS) analysis was carried out on annealed micron thick films of blends of C1(4CF)10K in bulk polystyrene at concentrations of 0.3, 1.0, and 3.0 wt %; the results are shown in Figure 8. The small peak at ∼770 keV confirms the presence of fluorine at the sample surface, which is clearly present at a greater concentration than in the bulk film.

The fluorocarbon peak is well separated from the signal due to oxygen at ∼650 keV and carbon at 450 keV. The films were sufficiently thick to prevent the incident beam from reaching the silicon substrate; therefore, there is no signal due to Si detected. Data for model simulations, in which the RBS spectrum of a thin layer of the fluorocarbon initiator C2, on a thick layer of polystyrene are shown as curves in Figure 8. Simulations were carried out using the SIMNRA program[63] and the quantity of fluorocarbon functional group in the simulation fitted to the experimental data to obtain the surface excess concentration. The experimental setup was designed to minimize any beam damage effects, which would if anything reduce the apparent surface concentration of fluorocarbon. A very small background contribution was detected at recoil energies greater than 800 keV due to residual traces of Br. By assuming that the Br concentration was constant throughout the bulk phase below the near surface region of the film, it was possible to include this contribution in the model profiles used to quantify the fluorine surface signal. The surface concentration of $C_8F_{17}$ fluorocarbon derived from the RBS analysis was 0.43, 0.89, and 1.18 mg m$^{-2}$ for the 0.3, 1.0, and 3.0% (w/w) C1(4CF)-10K blends, respectively. If one assumes that the $C_8F_{17}$ fluorocarbon groups lie parallel to the film surface, then each has an effective surface area of ∼0.7 nm$^2$. In this orientation, the surface excess concentrations correspond to 39%, 79%, and (105%) in increasing order of concentration. The uncertainty of the surface excess values is approximately ±15%; therefore, the value obtained for the 3% blend does not preclude the possibility of horizontally aligned fluorocarbon groups. The RBS analysis clearly shows that the functionalized polystyrene is highly surface-active, even at low concentrations in blends with unfunctionalized polystyrene. The derived surface concentrations are consistent with the contact angle analysis in that they confirm that the blend surfaces are highly fluorinated, even at low bulk concentrations. The resolution of RBS is not sufficiently good to probe the orientation of the fluorocarbon groups directly, so it is not possible to probe the fractional coverage accurately with this technique. However, it is notable that the fractional coverage inferred by assuming that $C_8F_{17}$ groups are horizontally aligned is close to 100%. However, in reality the likelihood is that even at the highest concentration of C1(4CF)10K the additives do not present a uniform surface of $CF_3$ groups. The block copolymers studied by Ober and Kramer contained an isoprene block of maybe a 100 repeat units decorated with up to 150 fluoroalkyl groups, resulting in a very densely packed fluoroalkyl surface and resultant contact angles greater than 120° in some cases. The presence of a pendant polymer chain attached to an end group containing at most 4 fluoroalkyl groups is not likely to form such a dense environment of fluoroalkyl groups at the surface. It is more likely that there is a distribution of orientations of the fluoroalkyl groups and possibly some spaces; however, the resulting maximum contact angles of 110−113° compare very favorably and possible exceed that of PTFE.

Intriguingly, the RBS data for the highest concentration (3%) of C1(4CF)10K revealed a secondary peak at ∼740 keV, too high in energy to be due to elements lower in mass than fluorine and of similar magnitude to the fluorine surface peak. This suggests that a second distinct layer rich in fluorine lies just below the film surface. The model fit to the RBS data was obtained by including a second fluorocarbon-rich layer beneath the film surface with an interstitial layer of dPS. The thickness of the interstitial dPS layer was fitted and found to be ∼11 nm thick and would suggest that at comparatively high bulk concentrations C1(4CF)10K may self-assemble at the film surface into lamellar structures. One would assume that self-assembly of additives in the bulk phase might also occur, and this observation/behavior is consistent with the discovery of multilamellar vesicles in the bulk of these blends by SANS and TEM and will be discussed in a companion paper elsewhere.

## Conclusions

We have synthesized a series of fluoroalkyl-functionalized ATRP initiators carrying 2, 3, and 4 fluoroalkyl groups and have successfully used these to polymerize both polystyrene and poly(methyl methacrylate). The polymerization of both monomers, using initiators with 2 and 3 fluoroalkyl groups, resulted in well-defined polymers with good agreement between expected molecular weights and molecular weights obtained by size exclusion chromatography. However, the use of an initiator with 4 fluoroalkyl groups only resulted in well-controlled polymerizations for lower molecular weights, up to 20 000 g $mol^{-1}$. Attempts to prepare polymers with higher molecular weights with this initiator resulted in poorer agreement between predicted and observed molecular weights; yields were reduced, and only about 50% conversion of monomer resulted. Kinetic plots for the polymerization of MMA showed in all cases that propagation initially proceeds with first-order kinetics with respect to monomer concentration but with some deviation from first order in the latter stages. The use of an initiator with 4 fluoroalkyl groups resulted in a marked reduction in the rate of propagation probably resulting in great chain termination.

The resulting end-functionalized polymers were blended in various concentrations with bulk polymer and films produced by spin-coating. The ability of the additives to migrate to the air−polymer surface and to modify surface properties was demonstrated by contact angle measurements using both water and dodecane as the contact fluid. The results showed that even the addition of small amounts of additive (1 wt %) caused measurable increases in contact angle with both contact fluids, and the addition of ∼10 wt % additive resulted in apparent saturation of the surface with additive molecules; the addition of higher concentrations showed little or no improvement in surface properties. In the case of polystyrene, increasing the number of fluoroalkyl groups from 2 to 3 to 4 resulted in a concomitant significant improvement in surface properties. Maximum contact angles for an additive with 2CF groups were 105° and 35° for water and dodecane, respectively, while for a near identical molecular weight polystyrene additive with 4 CF groups the maximum contact angles were 110° (water) and 65° (dodecane). These data show that we are generating surfaces with PTFE-like properties through the addition of a few percent by weight of fluoroalkyl groups. Somewhat unexpectedly, annealing the films for 1 h above the glass transition point for polystyrene offered only a slight increase in contact angles, implying that these additives are so surface-active that they spontaneously segregate to the surface during the spin-coating process. Fluoroalkyl-end-functionalized PMMA additives similarly modified the surface of bulk PMMA to substantially increase the hydrophobicity and oleophobicity.

Rutherford backscattering analysis of films containing C1-(4CF)10K allowed quantitative measurement of fluorine concentration at the surface, and even at 0.3% of additive there is a clear surface excess concentration with respect to the bulk. At 3% of additive a secondary peak in the RBS spectrum suggests the presence of a second fluorine-rich layer just below the surface.

Work is ongoing to optimize the structure of these additives with respect to molecular weight and number of fluoroalkyl groups as well as utilizing these end groups to functionalize other polymers prepared by a variety of mechanisms. We are also further investigating parameters such as concentration of additive and annealing conditions with a view to maximizing the surface modification with the use of the minimum amount of additive. Alternative methods of product formation to spin-coating are also under examination, including solvent-casting, electospinning of fibers, and extrusion. Our ultimate goal is to develop a versatile, facile, and cost-effective way of modifying the surface properties of the widest variety of polymers for a diversity of applications.

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